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High-speed GC/MS Using Narrow-bore Columns and Ion Trap Detection

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Abstract. Fast gas chromatographic separations can be achieved by vacuum-outlet operation and by applying narrow-bore columns. In this work, the combination of 50 μm i.d. columns with ion trap mass spectrometric detection is evaluated. Detection limits in the electron ionization mode, and in the chemical ionization mode using CH_4 as the reaction gas, are 1 pg and 5 pg, respectively. Owing to the high sensitivity of the ion trap mass spectrometer, a significant improvement in the working range in comparison with other detection systems is obtained. The small column flows cause no loss of mass spectral resolution and sensitivity. The performance of the system is demonstrated by the analysis of some real-world samples.

Key words: *capillary GC, narrow-bore columns, GC/MS, ion trap mass spectrometry, detection limits, working range*

INTRODUCTION

The reduction of the analysis time has been an important research topic in capillary gas chromatography (GC) ever since the introduction of open tubular columns by Golay in 1957 [1]. The first studies on minimal time operation in GC were presented by Desty and by Giddings in 1962. Desty *et al.* demonstrated that a reduction in the column inner diameter is an efficient means of reducing the analysis time [2]. Giddings emphasized the importance of the column pressure drop [3]. According to Giddings, the optimal performance can only be achieved under vacuum-outlet conditions. Schutjes demonstrated both theoretically and experimentally that the retention time in isothermal analysis is directly proportional to the column diameter in the case of large pressure drops. In the case of lower pressure drops, the retention time decreases proportionally to the square of the column diameter [4]. Noij studied the influence of the column diameter on the detection limits of the chromato-

graphic system [5]. The main conclusion from his work was that the minimal detectable amount is favored by the reduction of the inside diameter of the chromatographic column. In order to obtain lower minimal detectable concentrations, however, it is more advantageous to apply larger-bore columns.

Apart from the advantages described above, the use of narrow-bore columns also has a number of disadvantages. First, the sample capacity of the column is relatively low [6]. Moreover, in high-speed capillary GC, very narrow peaks are obtained. Hence, extra column peak broadening due to instrumentation must be minimized. The lack of adequate equipment has been a major obstruction for the successful use of narrow-bore columns. Considerable effort has been devoted to the development of compatible instrumentation for high-speed GC. These efforts have mainly focused on the development of injection devices capable of
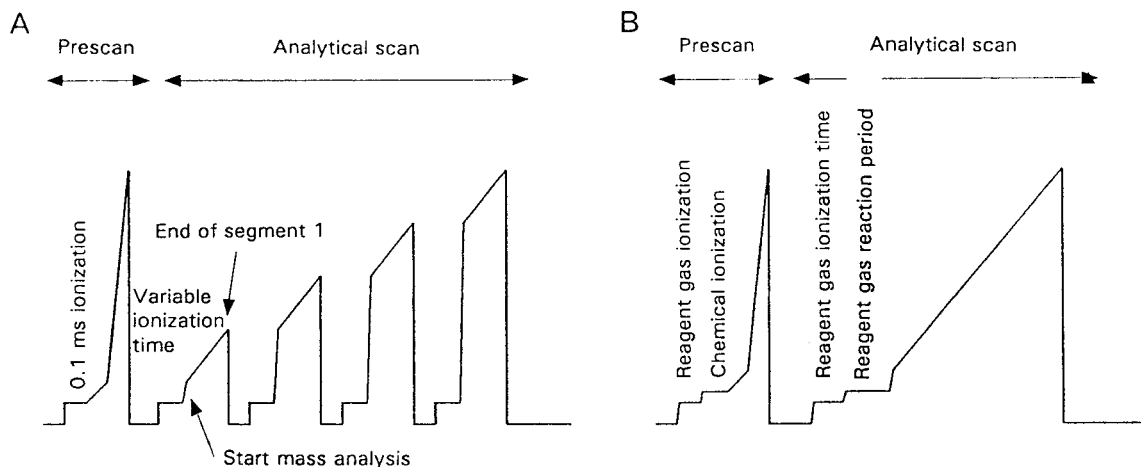
Figure 1. (A) Automatic gain control scan function; (B) automatic reaction control scan function.

introducing extremely small sample amounts with very narrow input bands.

Also with regard to the detector, some work has been done. Van Es investigated the performance of a number of GC detectors in combination with narrow-bore columns [7]. The combination of 50 μm i.d. columns with a quadrupole mass spectrometer [8] and a double focusing mass spectrometer with a focal plane array detector [9] has been evaluated by our group. The combination of narrow-bore columns with mass spectrometry (MS) is without any doubt one of the most powerful hyphenated techniques. In this respect, however, quadrupole instruments suffer from a number of important disadvantages, the most important ones being the limited sensitivity in the full scan mode and the relatively long time required to complete a spectral scan. Ion trap mass spectrometers appear highly promising for interfacing with narrow-bore columns, since these instruments are inherently more sensitive and faster than quadrupole instruments.

In this work, the combination of high-speed narrow-bore capillary gas chromatography with an ion trap mass spectrometer is evaluated. The mass detection limits in both the electron (EI) and chemical ionization (CI) modes have been studied. Special attention was paid to the sample capacity and the dynamic range. The influence of the instrument parameters (target and emission current) on the sensitivity and the quality of the mass spectra has been investigated in both the EI and CI modes. The performance of the system is demonstrated by several high-speed applications from industrial and environmental origin.

EXPERIMENTAL

The system used consisted of a Varian 3400 gas chromatograph (Varian, Walnut Creek, CA, USA) and an ion trap mass spectrometer (Varian Saturn II GC/MS). The chromatograph was equipped with an 8100 autosampler and a 1077 split/splitless injector. To allow operation at high inlet pressures, a Tescom 44-1100 high pressure regulator (Tescom, Minneapolis, MN, USA) and a custom-made digital pressure indicator were installed in the carrier gas line. The system was operated in the pressure controlled mode. The injector and the GC/MS transfer line were maintained at 275°C. Instrumental control and data processing were performed using the Varian Saturn software which ran on a Compaq PC (386-20e).

The fundamental principles and developments in ion trap MS have been reviewed by Todd in 1991 [10]. After ionization, the ions are trapped in the ion trap until they are ejected according to their mass-to-charge ratios. In the earlier versions of the ion trap, spatial charge interactions caused by high ion concentrations in the trap resulted in reduced linearity and loss in mass resolution, especially at high concentrations of the compound. A first improvement was introduced by Syka et al. [11] by making use of an axial modulation voltage (7 V). The space charge perturbation can also be reduced with a controlled scan function: the automatic gain control (AGC) in the EI mode and the automatic reaction control (ARC) in the CI mode (Figures 1A and 1B). In a prescan, the variable ionization time and reaction time (in the CI mode) are calculated to adjust the ion concentration in proportion to the target value (TV). In doing so, not only the space-

charge perturbation is minimized but also the sensitivity is increased approximately 50 times.

A 3 m x 50 μm i.d. DB-1 column (Fisons, J&W Scientific, Folsom, CA, USA) with 0.17 μm film thickness was used to determine the detection limits in the EI mode. A shorter DB-1 column (1 m x 50 μm i.d.) with a film thickness of 0.05 μm was used in the CI mode. In all of the experiments, an injection volume of 1 μL and a split ratio of 1:500 were used. The column temperature was 90°C. The scan range was 40 to 180 amu in the EI mode and 50 to 200 in the CI mode. Eight scans per s were obtained. In the EI mode, the number of scans were maximized by selecting the mass at the end of the first scan segment (200 amu) higher than the highest mass of interest. Then only one analytical scan segment is needed to complete the scan [12]. With the Saturn software, the maximal number of scans is limited to 10 per s.
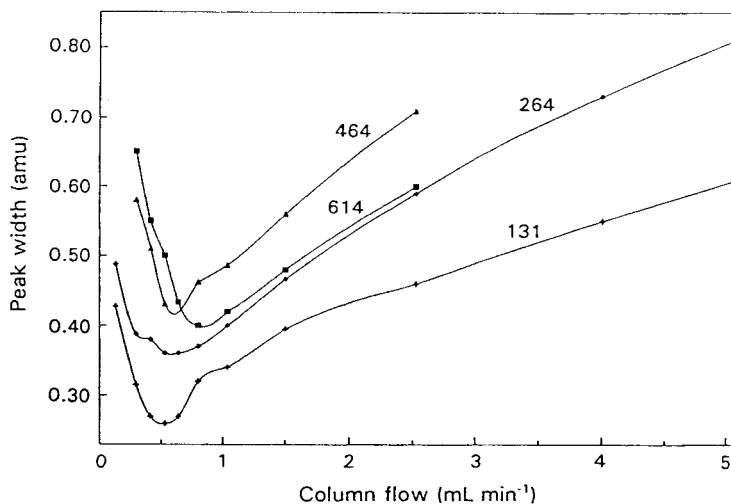
The influence of the helium flow on the mass resolution was evaluated by studying the widths of the mass peaks of the ions from the FC-43 calibration gas. The effect of the helium flow on the response was evaluated by injecting a mixture of alkanes from n-C_{13} to n-C_{16} diluted in hexane at different flow rates. The separations were performed with the 1 m DB-1 column at a temperature of 125°C.

Figure 2. *Peak widths measured at half height of some masses of the FC-43 calibration gas as functions of the column flow rate.*

Figure 3. *Responses (area counts) of n-C_{13} and n-C_{16} as functions of the column flow rate.*
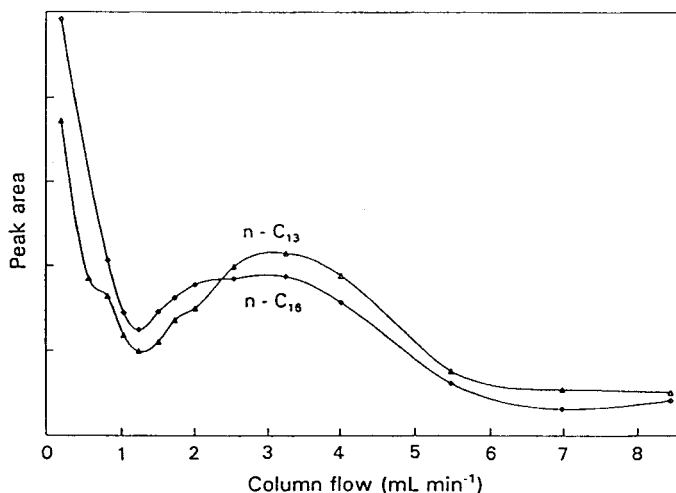
RESULTS AND DISCUSSION

Instrumental parameters. Optimization of the instrument control parameters was performed on the basis of measured peak areas and noise levels at various filament emission current (FEC) and TV settings. In the EI mode, both the signal and noise increase with increasing FEC. The best signal-to-noise ratio was obtained with an FEC of 30 μA and an AGC-TV of 30,000.

In the CI mode, the FEC was set at 10 μA. The peak heights were virtually independent of the TVs, while the lowest noise level was observed for high ARC-TVs (60,000).

Background pressure of helium, mass resolution, and sensitivity. As opposed to the situation in

quadrupole MS, the maximal mass resolution with ion trap detectors is obtained at relatively high helium background pressures. According to Stafford *et al.* [13], carrier gas ions tend to stabilize the trajectories of the sample ions in the ion trap, which results in increased mass resolution and improved sensitivity.

For 50 μm i.d. GC columns, typical (optimal) gas flows are approximately 0.5 mL min^{-1} (measured under ambient conditions). To test whether this relatively low helium flow would suffice for stabilization of the trapped ions, a series of experiments were performed at different helium flows. Under each of the conditions, the mass resolution

Table I. *Detection limits (pg) and working range in the EI and CI modes.*

| Analyte	EI mode	CH_4 CI mode	Isobutane CI mode
Decane	0.69	4.98	157
2,2,3,3-Tetramethylhexane	0.88	4.80	160
1-Chlorooctane	1.35	4.48	188
2-Nonanone	1.51	5.26	90
Undecane	1.43	6.56	159
2,4-Dimethylphenol	1.64	6.95	-
tert-Butylbenzene	1.47	-	-
Cymene	1.41	-	-
Working range	2500	500	10 to 25

and response were measured. The experimental results of these studies are shown in Figures 2 and 3. The flow rates under atmospheric conditions were calculated from

$$F_{out,atm} = \frac{\pi}{4} d_c^2 \bar{u} \cdot$$
$$\left[\frac{273.15 + T_r}{273.15 + T_o} \right] \left[\frac{2 P_i}{3 P_{atm}} \right] \quad (1)$$

where d_c is the column inner diameter, T_o is the temperature of the oven, and T_r is the temperature of the laboratory environment.

A minimal ion peak width was observed at a flow rate of 0.5 mL min^{-1}, which exactly equals the minimum of the H-u curve for the 50 μm i.d. column used in this study. At lower flow rates, the widths of the ion peaks increased rapidly, most likely because there were not sufficient helium ions for stabilization of the trajectories of the analyte ions. At higher flow rates and, hence, higher pressures in the trap, the ion trajectories were disturbed by collisions between ions and neutral molecules. This caused the mass resolution to decrease again.

To evaluate the influence of the helium background pressure on sensitivity, the peak areas of a number of test components were measured as functions of the column flow rate. At flow rates below 1 mL min^{-1}, the response increased sharply. The exact reason for this observation is yet unknown. The decrease in response observed at higher flow rates was most likely due to less efficient trapping at higher collision rates with helium molecules. The noise level was found to
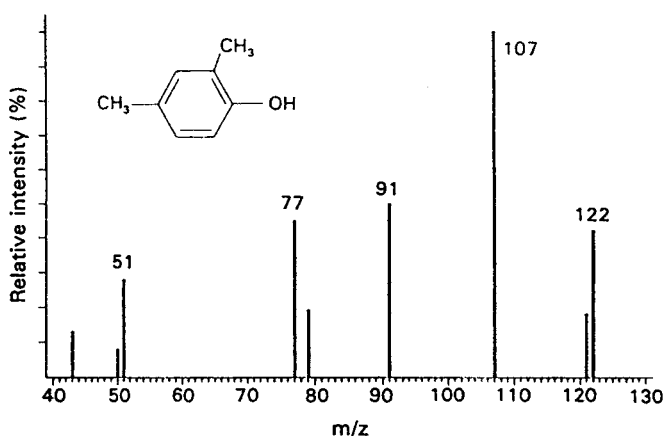

Figure 4. *Mass spectrum from 2.4 pg of 2,4-dimethylphenol (with background subtraction).*

remain constant for helium flows of up to 3 mL min^{-1}, but it increased sharply at higher flow rates.

Detection limits and dynamic ranges. The detection limits were calculated according to the equation [5]

$$Q_o^m = \sqrt{2\pi} \; \frac{4 R_n}{S} \; \sigma_t \quad (2)$$

where Q_o^m is the minimal detectable amount for a mass flow sensitive detector, R_n is the noise level, S is the sensitivity, and σ_t represents the band width of the analyte peak. A summary of the minimal detectable amounts is given in Table I. The chromatographic peaks eluting from the narrow-bore 50 μm i.d. column typically had peak widths (σ) in the 100 to 300 ms range. On a conventional 320 μm i.d. column, approximately 10 times wider peaks would be obtained. Hence it is clear from Equation 2 that narrow-bore columns
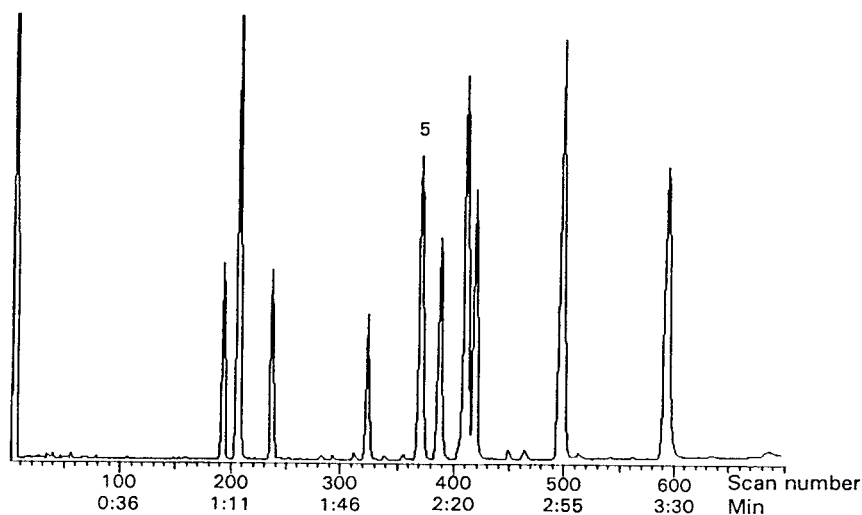
Figure 5. *High-speed chromatogram (TIC) of a mixture of liquid crystals. Conditions: 1 m x 50 μm i.d. column coated with DB-1 (0.05 μm d_f); temperature programmed from 140°C to 300°C at 40°C min^{-1}; 5 atm inlet pressure; 70 eV EI, 0.35 s scan^{-1}, 50-650 amu mass range.*

have a significantly lower mass detection limit than conventional columns.

As can be seen from Table I, the detection limits were approximately 1 pg in the EI mode. Under CI conditions with CH_4 as the reaction gas, the detection limits were approximately 5 times higher. In quantitative analysis, not only good detection limits, but also a wide linear dynamic range is important. Quantification is greatly simplified if the detection system exhibits a linear response over a wide range of concentrations. To evaluate the linearity of the gas chromatograph/ion trap combination, various samples with increasing concentrations were injected. At injected amounts (on the column) exceeding 2 to 3 ng, ill-shaped, leading peaks were observed. These peak shapes were clearly caused by overloading of the GC column. Therefore, it can be concluded that the working range, *i.e.*, the ratio of the amount where overloading of the column starts to occur over the minimal detectable amount of the narrow-bore GC/MS combination, was approximately 2.5×10^3 in the EI mode. Over this entire range, a linear detector response was observed. The working range in the CI mode was smaller and strongly dependent on the reagent gas.

As can be seen from Table I, the minimal detectable amount attainable with isobutane as the CI gas was about 30 to 40 times worse than with methane. Because of the poor sensitivity under isobutane CI conditions on the one hand, and the
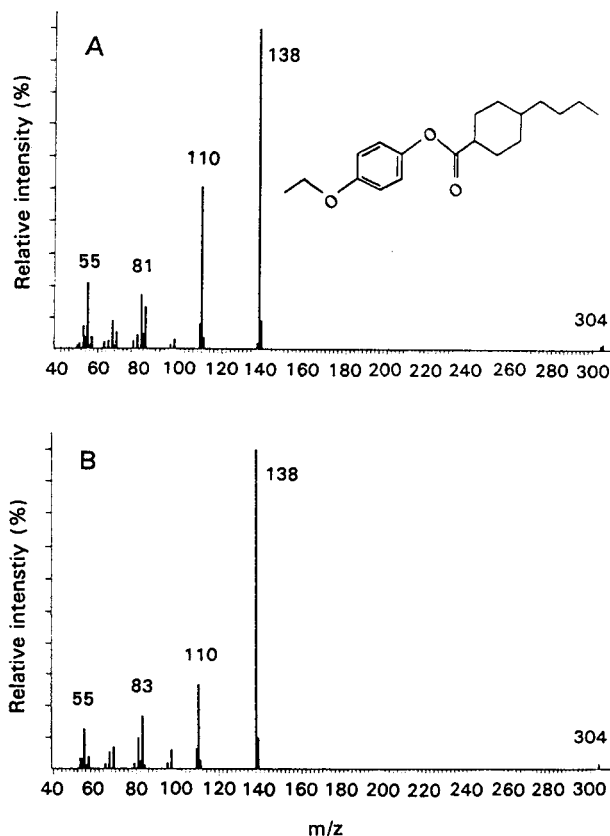

Figure 6. *(A) Experimental mass spectrum of peak 5 in Figure 5; (B) library mass spectrum of this component.*

limited sample capacity of narrow-bore columns on the other, the working range in the CI mode, using isobutane as the reagent gas, is too low for many practical applications. Here it must be emphasized
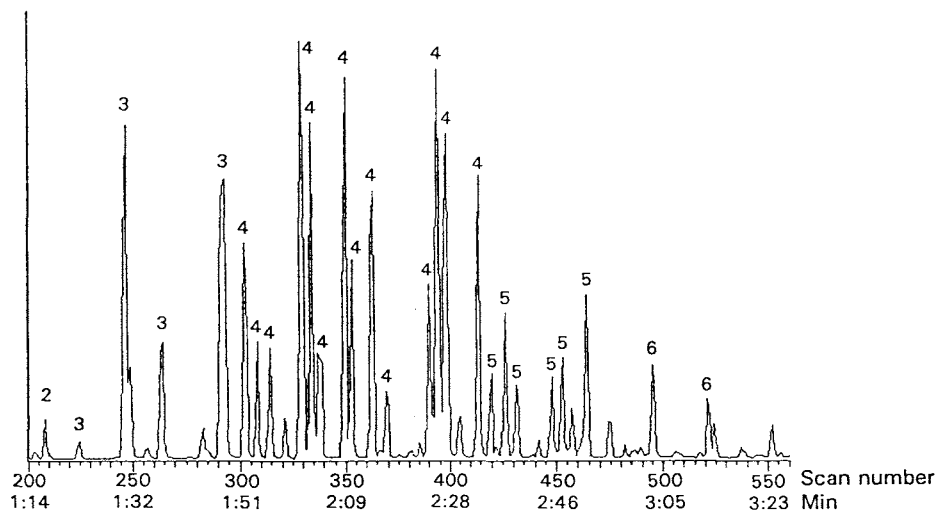
Figure 7. *High-speed chromatogram (TIC) of a PCB mixture (Arochlor 1248) in $CHCl_3$. Conditions: 7 m x 50 μm i.d. column coated with DB-1 (0.05 μm d_f); temperature programmed from 150°C to 300°C at 25°C min^{-1}; 15 atm inlet pressure; 70 eV EI, 0.35 s $scan^{-1}$, 50-650 amu mass range.*
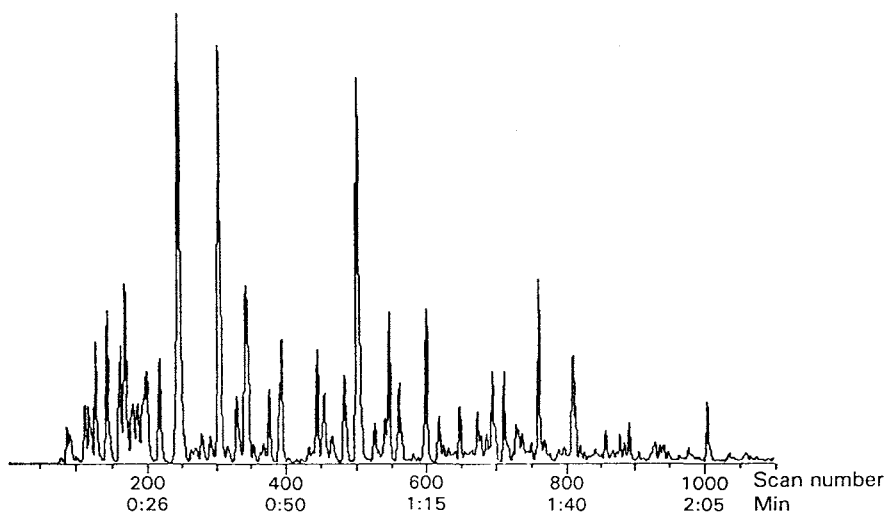
Figure 8. *High-speed chromatogram (TIC) of naphtha standard reference mixture (No. 4-8265). Conditions: 7 m x 50 μm i.d. column coated with DB-1 (0.05 μm d_f); temperature programmed from 35°C to 200°C at 40°C min^{-1}; 20 atm inlet pressure; CH_4 CI, 0.125 s $scan^{-1}$, 50-230 amu mass range.*

that a direct comparison of the linear dynamic ranges observed under EI and CI conditions is not valid since the stationary phase film thicknesses of the columns used in the two series of experiments are not identical.

Mass spectra. In the first generation of ion trap detectors, introduced a decade ago, the mass spectra strongly depended on the amount of solute introduced onto the column. Large differences in the relative ion abundances were even observed in subsequently acquired mass spectra from one peak. The influence of the operational conditions on the mass spectra obtained with an ion trap mass spec-

trometer has been the subject of a number of research papers [12,14-16]. The main reason for the distortion of the spectra obtained with the earlier instruments was the occurrence of space charging during the relatively long residence times of the ions in the ion trap. In this respect, the use of narrow-bore columns in combination with ion trap MS detection might be advantageous because of the minute sample quantities that elute from the column. Due to the high sensitivity of the ion trap, a reasonable working range is preserved despite the low sample capacity of the narrow-bore GC columns.

For a wide variety of components including some esters, phenols, ketones, chlorinated alkanes, *etc.*, the variation of the FEC and the TV caused no differences in the mass spectra. The small variations (a few percent) of the relative abundances in the mass spectra, due to the variation of the sample amount in the trap, caused no problems in identification of the compounds. In Figure 4, the spectrum of 2,4-dimethylphenol collected for a sample amount of no more than 2.4 pg is presented. Even these small amounts can successfully be identified with a library search.

Applications. The combination of narrow-bore columns with ion trap MS detection is an attractive hyphenated technique for a large number of high-speed applications.

In Figure 5, an example of the high-speed separation of a liquid crystal mixture is presented. The analysis of this mixture with a 0.32 mm i.d. column (generating the same plate number) takes approximately 1 h. The larger peaks correspond to approximately 0.5 ng. For the later eluting components, peak overloading and broadening already start to occur, illustrating the extremely low sample capacity of narrow-bore columns. In Figure 6A, the mass spectrum of peak 5 from Figure 5 is presented. Figure 6B shows the library spectrum of this component. As can be seen from this figure, the experimental mass spectrum closely resembles the library spectrum.

Another interesting application is the analysis of the PCB mixture, Arochlor 1248. Here the separation of this complex mixture is achieved in less than 4 min. A similar separation on a conventional 320 μm i.d. column would take approximately 30 to 40 min. With mass chromatography, the clusters of PCBs containing equal numbers of chlorine atoms can be readily identified. In Figure 7, the number of chlorines on the biphenyl moiety is shown at the top of each peak.

An example of a combination of a high-speed GC analysis and CI with CH_4 as the reagent gas is presented in Figure 8. This figure shows the analysis of a naphtha reference mixture (No. 4-8265, Supelco, Bellefonte, PA, USA). The sample contains a mixture of alkanes ranging from C_3 up to C_{12}, including a series of aromatic constituents.

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